

# Disorder-assisted melting and the glass transition in amorphous solids

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The mechanical response of solids depends on temperature because the way atoms and molecules respond collectively to deformation is affected at various levels by thermal motion. This is a fundamental problem of solid state science and plays a crucial role in metallurgy, aerospace engineering, energy. In glasses the vanishing of rigidity upon increasing temperature is the reverse process of the glass transition. It remains poorly understood due to the disorder leading to nontrivial (nonaffine) components in the atomic displacements. Our theory explains the basic mechanism of the melting transition of amorphous (disordered) solids in terms of the lattice energy lost to this nonaffine motion, compared to which thermal vibrations turn out to play only a negligible role. It predicts the square-root vanishing of the shear modulus  $G \sim \sqrt{T_c - T}$  at criticality observed in the most recent numerical simulation study. The theory is also in good agreement with classic data on melting of amorphous polymers (for which no alternative theory can be found in the literature) and offers new opportunities in materials science.

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The phenomenon of the transition of a supercooled liquid into an amorphous solid has been studied extensively and many theories have been proposed in the past, starting with the Gibbs-DiMarzio theory [1]. All these theories focus on the fluid to solid aspect, coming to this glass transition from the liquid side (supercooling). However, it is only one facet of the problem. For the reverse process, i.e. the melting of the amorphous solid into a liquid, no established theories are available.

The problem of describing the melting transition into a fluid state [2–9] is complicated in amorphous solids by the difficulties inherent in describing the elasticity down to the atomistic level (where the thermal fluctuations take place). It is well known that the standard (Born-Huang) lattice-dynamic theory of elastic constants, and also its later developments [10], breaks down on the microscopic scale. The reason is that its basic assumption, that the macroscopic deformation is *affine* and thus can be down-scaled to the atomistic level, does not hold [11]. Atomic displacements in amorphous solids are in fact strongly *nonaffine* [11–14], a phenomenon illustrated in Fig. 1. Nonaffinity is caused by the lattice disorder: the forces transmitted to every atom by its bonded neighbors upon deformation do not balance, and the resulting non-zero force can only be equilibrated by an additional nonaffine displacement, which adds to the affine motion dictated by the macroscopic strain.

Recently, it has been shown [15] that nonaffinity could play a role in the melting of model amorphous solids, although the basic interplay between nonaffinity, thermal expansion, and thermal vibrations remains unclear. With a number of other models of the glass transition, such as mode-coupling theories, there is also an issue when they rely on liquid-state theory for relating the stress tensor to local fluctuations in the solid state. These theories predict that the shear modulus  $G$  of *athermal* hard-sphere colloids remains finite at the glass transition [16] and

that it jumps discontinuously to zero upon decreasing the packing fraction  $\phi$ . This scenario does not agree, however, with *thermal* systems, where both simulations [17] and experiments [18] show that the vanishing of  $G$  is continuous with  $T$ . The glass transition temperature  $T_c$  could therefore be estimated for thermal systems using the Born melting criterion [2], i.e. setting  $G(T) = 0$  [19] and solving for  $T_c$ , if a theory for the low-frequency  $G$  in the solid state is available.

Here we discover a much more basic effect that non-affinity of deformation causes in the melting, where marginal stability controls the response through the bond-connectivity, in turn affected by both  $T$  (via thermal expansion) and disorder. The resulting framework allows us to link lattice disorder, connectivity and thermal vibrations into the first description of the classical experiment [20] on  $T$ -dependent low-frequency shear modulus of amorphous polymers.

Let us start from the basic assumptions of Born-Huang lattice dynamics [2]. The free energy density of affine deformation is given by the following harmonic lattice sum:  $F_A = \frac{1}{2V} \sum_{ij} (\partial^2 U / \partial r_{ij}^2)_{R_0} (\underline{u}_{ij}^A)^2$ , which runs over all bonded atom pairs  $ij$ . Here  $U(r_{ij})$  is the pair-interaction potential and the vector  $\underline{u}_{ij}^A = \underline{r}_{ij}^A - \underline{R}_{ij} = \underline{\eta} \cdot \underline{R}_{ij}$  denotes the affine displacement, with  $\underline{\eta}$  the macroscopic strain tensor and  $\underline{R}_{ij}$  the bond vector in the undeformed frame.  $R_0$  is the equilibrium lattice constant in the undeformed frame, at which one evaluates the lattice spring constant  $\kappa = (\partial^2 U / \partial r_{ij}^2)_{R_0}$ . Without loss of generality, we focus on *shear* strain  $\eta_{xy} \equiv \gamma$ . The lattice sum can be evaluated upon introducing the average number of bonds per atom  $z$ , and in the affine approximation [21]:  $F_A = \frac{2}{10\pi} (\kappa / R_0) \phi z \gamma^2$ . Here  $\phi = vN/V$  is the packing fraction occupied by the atoms or building blocks of the solid.

In general, the contribution to  $F$  due

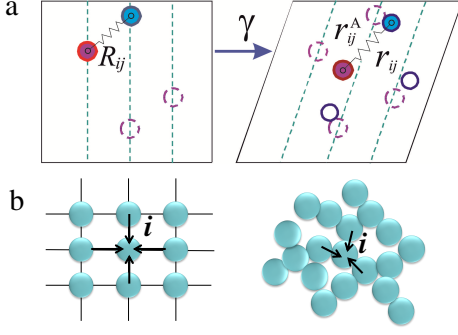


FIG. 1: **a**, If the deformation was affine, the particles labeled with darker color would still lie on the dashed lines also in the deformed (right) frame. Because of nonaffinity, they do not. **b**, In an ordered crystal lattice (left) the forces (arrows) transmitted to any particle  $i$  by its nearest neighbors upon deformation cancel each other and the net force acting on  $i$  is zero by symmetry. In a disordered lattice (right) the forces transmitted upon deformation do not balance, and a net force acts on  $i$  which has to be balanced by a nonaffine motion, to further lower the lattice potential energy in order to preserve the mechanical equilibrium.

to thermal phonons is given by:  $F_T = -kT \ln \sum_n^\infty \exp(-\hbar\omega_n(n + \frac{1}{2})/kT)$ , where  $n$  labels the eigenmodes. If  $kT \gg \hbar\omega_{\max}$ , one has:  $F_T = -(3N/V)kT \ln(kT/\hbar\bar{\omega})$ , where  $\bar{\omega}$  is defined such that  $\ln \bar{\omega}$  is equal to the average value of  $\ln \omega$ . The contribution of the thermal phonons can be written as:  $F_T \approx -(3N/V)kT\theta\gamma^2$  where the non-dimensional factor  $\theta = -(\partial^2/\partial\gamma^2)_{\gamma \rightarrow 0} \ln \hbar\bar{\omega}/kT$  has been demonstrated [9] to be of order unity when the harmonic potential dominates the pair interaction potential. This gives a good estimate:  $F_T \approx -(3N/V)kT\gamma^2$ .

The number of mechanical bonds per atom  $z$  requires a careful definition in amorphous thermal systems. If there were only covalent bonds, then  $z$  is obviously just equal to the number of covalent bonds per atom. However, in addition to covalent bonds, weaker interactions are present, such as those between two monomers of different chains in polymer systems. Such interactions are of van der Waals nature and they can be modeled by the Lennard-Jones (LJ) potential. In that case, it is important to distinguish quantitatively between these contributions in the total  $z$ . Here we propose the following criterion that allows us to calculate these terms unambiguously. With a glassy polymer in mind (although without any loss of generality), we shall assume that a contribution to  $z$  arises from inter-chain interactions whenever the two monomers are at a mutual separation  $r \leq r_{\min}$ , where  $r_{\min}$  is the minimum of the LJ potential well, see Fig. 2. Although this procedure might slightly underestimate the actual absolute value of  $z$ , the underestimation has no effect on the change  $\delta z$  upon varying  $T$  which is the quantity that matters in our calculation. Later in the text, when we

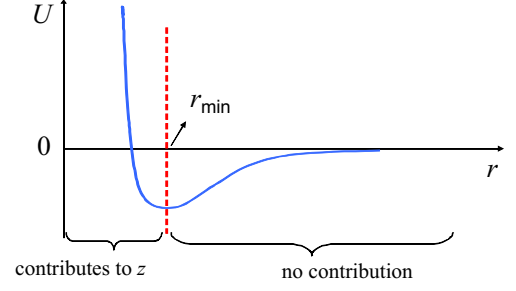


FIG. 2: Schematic of the criterion used to define the contribution of the weaker Lennard-Jones interactions to the total number of mechanical bonds  $z$ . Only pairs of particles that lie within the soft repulsive part of the potential (to the left of the minimum) contribute to the  $z$  counting.

compare the model predictions with a particular experiment on polymer glasses [20], we shall derive the explicit values for the two components contributing to the total average  $z$ : the one due to intra-chain covalent bonds  $z_{co}$  and the one due to inter-chain LJ bonds, which we denote  $z_{LJ}$ .

Having defined the total  $z$ , we now need to relate it to  $T$ . Upon introducing the thermal expansion coefficient,  $\alpha_T = \frac{1}{V} (\partial V / \partial T)$ , and replacing the volume  $V$  via  $\phi = vN/V$ , after integration we obtain  $\ln(1/\phi) = \alpha_T T + \text{const}$  (later we shall need to estimate this constant, obtaining  $C \sim 0.48$ ). Now  $z$  can be estimated as a function of  $\phi$  by introducing the radial distribution function (rdf)  $g(r)$ . Since the average connectivity due to covalent bonds remains fixed, only the weaker contact bonds contributing to  $z_{LJ}$  are changing upon increasing the packing fraction  $\phi$  by  $\delta\phi$ . The increment  $\delta z$  can be calculated in full analogy with soft-sphere systems where only the repulsive part of the potential is active. This increment is given by [22]:  $\delta z \sim \int_1^{1+\delta\phi} \xi^2 g(\xi) d\xi$ , where  $\xi$  is the normalized center-to-center distance. The rdf in the repulsive part is dominated by  $g(\xi) \sim \sqrt{\xi - 1}$ , as shown in theory [22] and simulations [23]. To keep things analytical, here we neglect the thermal broadening of the rdf (which could be calculated only using involved replica techniques [24]). This particular simplifying approximation should still work for relatively low- $T_c$  polymer glassy systems, as we are going to verify below, but certainly has to be adjusted when dealing with inorganic glasses which have an order of magnitude higher  $T_c$ . The increment  $\delta z$  has to be measured from the point where the system is marginally stable, i.e.  $z = z_c$  at  $\phi = \phi_c$ , and from the integral we obtain:  $z - z_c \sim \sqrt{\phi - \phi_c}$ . In the affine approximation, the solid becomes marginally stable only in the limit  $z_c \rightarrow 0$  and  $\phi_c \rightarrow 0$ , and hence we have  $z \sim \phi^{1/2}$ . Using the earlier relation between  $\phi$  and  $\alpha_T$  we obtain:  $z \sim e^{-\alpha_T T/2}$ . Substituting  $z$  and  $\phi$  in  $F_A + F_T$  we now can write the full expression for the shear modulus in the

affine approximation,  $G_A = \partial^2(F_A + F_T)/\partial\gamma^2$ , yielding:

$$G_A(T) = \frac{2}{5\pi} \frac{1}{R_0^3} (\kappa R_0^2 e^{-(3/2)\alpha_T T} - kT e^{-\alpha_T T}). \quad (1)$$

The Born criterion of melting [2], is given by Eq.(1) set to zero:  $\kappa R_0^2 = kT e^{\alpha_T T/2}$ . We shall see later that  $\alpha_T T \ll 1$  and, remarkably, this relation reproduces the Lindemann criterion [25], which uses equipartition to state that melting occurs when the average vibrational energy of a bond equals  $kT$ . The Lindemann criterion grossly overestimates melting temperatures for amorphous solids [11]; also, Eq.(1) cannot capture the vanishing of rigidity as seen in the melting of glassy polymers [20]. It turns out that to describe the melting of amorphous solids one has to account for nonaffine deformations in the lattice dynamics.

The shear modulus accounting for nonaffine deformations is derived in [26] as a lattice sum:  $G = G_A - G_{NA} = G_A - \sum_i \underline{f}_i \sum_j \underline{H}_{ij}^{-1} \underline{f}_j$ , where  $\underline{H}_{ij} = (\partial^2 F / \partial r_{ij}^2 \partial r_{ij}^2)_{\gamma \rightarrow 0}$  is the dynamical matrix of the solid. The vector  $\underline{f}_i$  measures the increment of force acting on an atom in response to the deformation (here  $\gamma \equiv \eta_{xy}$ ) of its environment. It can be shown that for harmonic pair potential [26]:  $\underline{f}_i = -R_{ij} \kappa \sum_j \underline{e}_{ij} e_{ij}^x e_{ij}^y$ , where  $\underline{e}_{ij}$  is the unit vector along the bond connecting two atoms  $i$  and  $j$ . Since the sum runs over bonds to the nearest-neighbors  $j$  of the atom  $i$ , it is evident that in a perfect crystal for each bond involving  $i$  there is a mirror-image bond across a reflection plane of the crystalline lattice. Therefore, every bond in the sum cancels with its mirror-image, and  $\underline{f}_i = 0$ ,  $\forall i$  in most crystal lattices. As a result,  $\underline{f}_i$  is nonzero only with lattice disorder, see Fig. 1b. The non-affine correction to the elastic free energy arises to ensure that mechanical equilibrium, which disorder tends to compromise, is preserved upon deformation. It has been evaluated, in mean-field approximation, for random assemblies of harmonically bonded particles [27, 28]:

$$G = G_A - G_{NA} = \frac{2}{5\pi} \frac{\kappa}{R_0} \phi(z - z_c). \quad (2)$$

It should be noted that this expression has been derived for harmonic pair potentials and is therefore valid for any potentials with an attractive minimum.

The nonaffine contribution is encoded in Eq. (2) in the term proportional to  $z_c$  which expresses the internal energy required to fuel the nonaffine motions necessary for the preservation of mechanical equilibrium against the effect of disorder. With purely central-force interactions in  $d$  dimensions, the shear modulus vanishes at  $z_c = 2d$  ( $z_c = 6$  in 3D) because the nonaffine term is proportional to the number of degrees of freedom that can be involved in the nonaffine energy relaxation. This is consistent with the classical Maxwell criterion for marginal stability with purely central forces:  $G \sim (z - 6)$ . In general,  $z_c$  defines the critical coordination at which the lattice is no longer

rigid because all the lattice potential energy is “spent” on sustaining the nonaffine motions and no energy is left to support the elastic response to deformation. Using again:  $\ln(1/\phi) = \alpha_T T + C$ , we arrive at:  $\ln(\phi_c/\phi) = \alpha_T(T - T_c)$ . The corresponding relation  $z - z_c \sim \sqrt{\phi - \phi_c}$  can be manipulated into:

$$\ln(\phi_c/\phi) = -\ln[1 + (z - z_c)^2/\phi_c]. \quad (3)$$

Combining this with the relation for  $\phi(\alpha_T)$  we obtain  $\ln[1 + (z - z_c)^2/\phi_c] = \alpha_T(T - T_c)$ , and finally arrive at the condition:  $z - z_c = \sqrt{\phi_c[e^{\alpha_T(T - T_c)} - 1]}$ . Substituting it in Eq.(2), we obtain:

$$G_A - G_{NA} = \frac{2}{5\pi} \frac{\kappa}{R_0} \phi_c e^{\alpha_T(T - T_c)} \sqrt{\phi_c[e^{\alpha_T(T - T_c)} - 1]}. \quad (4)$$

According to this equation for the shear modulus  $G(T)$ , nonaffinity alone (induced by disorder) causes the melting at a critical point  $T_c$  with the scaling  $\sim \sqrt{T_c - T}$ , even without the effects of thermal vibrations on the rigidity. Including the effect of thermal phonons in the same way as was done in Eq.(1), the full expression for  $G(T)$  becomes:

$$G = \frac{2}{5\pi} \left( \frac{\kappa}{R_0} \phi_c e^{\alpha_T(T - T_c)} \sqrt{\phi_c[e^{\alpha_T(T - T_c)} - 1]} - \frac{kT}{R_0^3} e^{-\alpha_T T} \right). \quad (5)$$

The square-root cusp singularity  $G \sim \sqrt{T_c - T}$  predicted by our theory for the shear modulus has been reported in the most recent numerical simulations for the melting of colloidal glasses [29] which thus confirm the validity of our approach. To assess the interplay and relative magnitude of nonaffinity and thermal phonons, it is important to have an expression for the critical point  $T_c$  in terms of parameters used in this analysis. Since  $T_c$  is, in effect, the glass transition temperature, the task of finding it explicitly for a general system remains challenging. However, since our comparison will be with a particular experimental system of polymeric glass, we can in fact offer an expression in such a case. For polymer chains of  $n$  units, the average connectivity due to intra-chain covalent bonds is close to 2:  $z_{co} = 2(1 - 1/n)$  (the total coordination number is  $z = z_{co} + z_{LJ}$ ). The LJ are central forces, but the covalent bonds also put a constraint on the bond angle. The classical Phillips-Thorpe analysis of marginal stability [30, 31] gives the fraction of floppy modes  $f = N_{\text{floppy}}/3N$  in a purely covalent network:  $f = 1 - \frac{1}{3} \left( \frac{1}{2} z_{co} + [2z_{co} - 3] \right)$ , where every  $z_{co}$ -coordinated monomer contributes  $2z_{co} - 3$  bending constraints, in addition to  $\frac{1}{2} z_{co}$  stretching constraints. In our case, upon adding the LJ inter-chain bonds into the counting, the fraction of floppy modes becomes:

$$f = 1 - \frac{1}{3} \left( \frac{1}{2} z_{co} + [2z_{co} - 3] + \frac{1}{2} z_{LJ} \right). \quad (6)$$

Keeping  $z_{co}$  fixed, since it is  $T$ -independent and fixed by the polymer chemistry, we set  $f = 0$  in the above

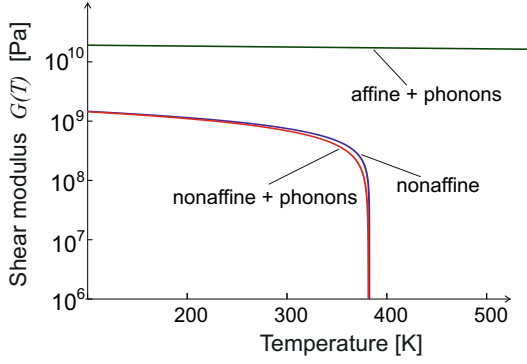


FIG. 3: Comparison of theoretical predictions from Eq.(5) (nonaffine + phonons), Eq. (4) (nonaffine athermal), and Eq. (1) (affine + phonons). We take  $T_c = 383\text{K}$ ,  $R_0 = 0.3\text{ nm}$ ,  $\alpha_T = 2 \cdot 10^{-4}\text{K}^{-1}$ , as for polystyrene,  $\phi_c = \phi_c^* - \Lambda \cdot z_{co} = 0.44$ , and the spring constant  $\kappa = 50\text{ N/m}$ .

equation and solve for the critical value of  $z_{LJ}$  at the rigidity transition, obtaining:  $z_{LJ}^* = 12 - 5z_{co}$ . Upon applying  $z_c = z_{co} + z_{LJ}^*$ , we obtain the critical value of the total connectivity  $z$  at which the rigidity is lost:  $z_c = 12 - 4z_{co} = 12 - 8(1 - 1/n)$ . In other words, in order for the amorphous polymer assembly to become solid (glass) there need to be at least  $z_{LJ}^* = z_c - z_{co} = 12 - 5z_{co}$  LJ inter-chain bonds per monomer, in addition to the chain connectivity. Now we convert  $z_c$  into the critical volume fraction  $\phi_c$ , via  $\phi_c = \phi_c^* - \Lambda \cdot z_{co}$ , where  $\phi_c^*$  is the packing fraction in the limit  $z_{co} = 0$ . If the attraction is weak or absent, as in a system of hard spheres, then  $\phi_c^* \simeq 0.64$  as for random packings.

Finally, using the expression for  $\phi_c(\alpha_T T)$ , and for  $z_{co}(n)$ , we obtain the glass transition temperature for chains with degree of polymerization  $n$ :

$$T_c = \frac{1}{\alpha_T} (1 - C - \phi_c^* + 2\Lambda) - \frac{2\Lambda}{\alpha_T n}. \quad (7)$$

The first term is what remains for very long chains ( $n \gg 2\Lambda/\alpha_T$ ). The expression (7) provides a theoretical foundation for the empirical dependence of the glass transition on  $n$ , first discussed by Flory [32, 33]. For common polymers, the experimental values of the factor  $2\Lambda/\alpha_T$  [32, 33] are of order  $10^3\text{K}$ , and hence  $\Lambda \simeq 0.1$ . If we take  $T_c \simeq 383\text{K}$ , as for polystyrene glass used in the experimental comparison below, this gives a reasonable value of  $C \simeq 0.48$ . This value implies that  $\phi \simeq 0.61 \cdot e^{-\alpha_T T}$ , in dense amorphous polystyrene.

In Fig. 3 we have plotted predictions of different theories for the shear modulus  $G(T)$  using the parameters of amorphous polystyrene, taking  $n = 200$  [20]. It is evident that nonaffinity is the main effect driving the melting transition, whereas thermal phonons have practically no effect on the qualitative behavior of the melting curve. On the other hand, if nonaffinity is neglected, the transition is shifted to unrealistic, enormously high temperatures.

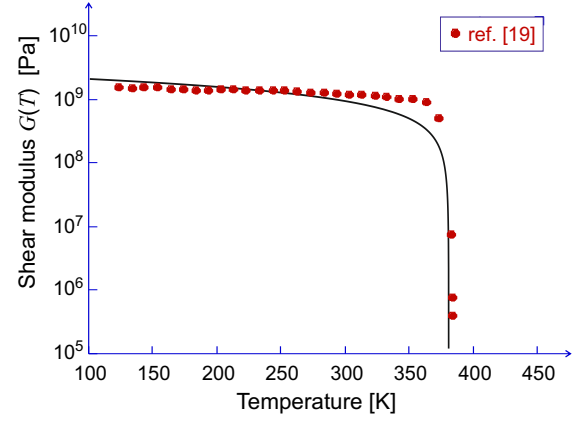


FIG. 4: Theoretical fit of the experimental data for amorphous polystyrene using Eq.(5) and the same values for parameters as in Fig.3, including  $T_c = 383\text{K}$ , and fitting for the single parameter: the spring constant  $\kappa = 52\text{ N/m}$ . The experimental data were taken at a constant frequency of  $0.9\text{ Hz}$ .

Finally, Fig. 4 shows the comparison of our theory prediction for the melting of amorphous polystyrene with the classical experimental data of Schmieder and Wolf [20], reported also in Ferry's monograph as representative of the quasistatic, low-frequency  $G(T)$  in the glassy solid state [34]. As discussed by Ferry, the catastrophic drop of  $G$  at the critical point is the hallmark of the low-frequency (static) response, whereas at higher frequency the drop becomes more gradual (due to the reduced non-affinity, from our point of view). Experimental data taken at even lower frequency would not differ much as the drop can hardly be sharper than in Fig. 4.

The value of the fitting parameter, the spring constant  $\kappa \approx 52\text{ N/m}$  is very sensible: it corresponds to the C-C covalent bond enthalpy  $350\text{kJ/mol}$  over a distance of  $0.15\text{ nm}$ , which is almost exactly the C-C bond length ( $0.146\text{ nm}$ ). More importantly, the theory can reproduce the qualitative behavior of the experimental curve and the criticality (that are found also with many other polymers [20, 34]) very well indeed. It is important to notice that no alternative theory is available in the literature for the mechanical response of amorphous polymers at  $T < T_g$  (in contrast, at  $T > T_g$ , the reptation theory of de Gennes, Doi and Edwards [35] provides a good understanding of viscoelasticity of polymer melts).

From the point of view of applications, our theory can be used to reconstruct the thermoelastic behavior of glassy polymers at  $T < T_g$ , something which has not been possible so far, in the same way as the Williams-Landel-Ferry theory [34] is used for the viscosity at  $T > T_g$ . The theory can be used to model also the melting curves of inorganic materials, such as amorphous oxides, semiconductors and metallic glasses where the thermal phonons play a more important role in view of the much higher  $T_c$ .

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